IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	B. Kim et al.	Attorney Docket No.: SEMT119849	
Application No.:	10/700,782	Art Unit: 1753 / Confirmation No: 5493	
Filed:	November 3, 2003	Examiner: E. Wong	
Title:	BATH AND METHOD FOR HIGH RATE COPPER DEPOSITION		

DECLARATION OF BIOH KIM UNDER 37 C.F.R. § 1.131

Seattle, Washington 98101

October 19, 2007

TO THE COMMISSIONER FOR PATENTS:

I, Bioh Kim, declare as follows:

1. I am an engineer residing in Milford, Connecticut, and a former employee of Semitool, Inc., the assignee of the above-identified application. In connection with and during the period of my employment with Semitool, Inc., I invented the claimed subject matter currently pending in the above-identified application.

2. I have reviewed the specification and the claims currently pending in the above-identified application. The claims are directed to a process for electroplating copper on a microelectronic workpiece in a through-mask plating application at a rate of at least 2 μm/minute.

3. Having reviewed the claims, I verily believe that I conceived and reduced to practice the subject matter falling within the claims currently pending in the above-identified application prior to March 30, 2001.

4. To demonstrate such conception and reduction to practice, I attach hereto as Exhibit A, an invention disclosure, attention specifically called to pages 12-13 and 16-19, which I prepared and signed (and which was witnessed by Zhongmin Hu) disclosing baths and methods for high rate copper deposition. With reference to these examples, FC99 includes a wetting

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agent (see, for example, page 12); Shipley B2001 includes a brightener (see, for example, page 13, column 2); and Shipley C2001 includes a leveler and a suppressor (see, for example, page 13, column 3).

5. Exhibit A lists dates of conception, written description, and first sketch or drawing (all redacted), all prior to March 30, 2001. In addition, Exhibit A lists the date that a working model was prepared (also redacted), which is also prior to March 30, 2001.

6. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and, further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: oct, 19th, 2007.

Respectfully submitted,

Bioh Kim

ECP:dmg

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EXHIBIT A

D01-0048

INVENTION DISCLOSURE

SEMITOOL, INC. D99-______

IN CASE OF MULTIPLE INVENTORS: GET PAGE 2 OF THIS DISCLOSURE; EACH INVENTOR MUST FILL OUT INVENTOR INFORMATION.

Note: 1. Use Ink or Type Only
2. Do not erase errors. Line through any errors, initial and date
3. Describe invention with drawings, sketches, etc. and a written explanation. Drawings may be below or attached. If attached, the inventor(s) and witnesses must sign and date each sheet.
4. Describe the advantages of this invention compared to the current approach, if any.
5. Inventor(s) and two (2) witnesses must sign and date each sheet
6. Send original signed documents to the Intellectual Property Department. Retain a personal copy.

Inventor's Full Name (include middle initial, jr., sr., I, II, etc.)
Bioh Kim

☐ **Check Box if there is more than one inventor (use page two of disclosure for additional inventors)**

Inventor's Physical Home Address: 117 Sunburst Ct, Kalispell, MT, 59901

Inventor's Citizenship: Seoul, Rep. of Korea

Title of Invention: Bath and method for high rate copper deposition for bumping application

Tool or Process: Semitool's Equinox or LT **Division: ATG** **If Other, describe:**

Invention:

Sketch, Explanation and Advantages: Refer to the attached.

Signature(s) of Inventor(s):	Date:	Date of Conception:	Date of First Sketch/Drawing:
[signature]	[redacted]	[redacted]	[redacted]
Witnessed and Understood By:	**Date:**	**Date of Written Description:**	**Working Model Prepared?**
Zhongmin Hu	[redacted]	[redacted]	☑ Yes / ☐ No Date: [redacted] ~ now

REDACTED

Bath and Method for High Rate Copper Deposition for Bumping Application

[redacted] Bioh Kim

The most commonly used solders for flip-chip application is eutectic lead-tin (63/37) alloy, eutectic tin-silver (96.5/3.5), eutectic tin-copper (99.3/0.7) and near-eutectic tin-silver-copper (Sn/3.5-4.5Ag/0.3-0.9Cu) alloys. In most cases, a thick copper layer, so-called copper mini-bump, is deposited to provide a wettable surface on the top of an unwettable diffusion barrier as well as to form a bonding layer through the reaction with the active element (tin) of the solder. Sn-Cu metallurgical intermetallic compounds are formed during the reflow process. Electrodeposition is the easiest and cheapest way to deposit a thick copper. The biggest shortcomings of this technology are the process time required to deposit thick copper bumps and the incorporation of additives in the film.

To date, the deposition rate of 0.4~1.0 um/min, which is not enough for bumping applications, is generally achievable with the commercial copper bath for interconnect (such as via, trench, and dual damascene) applications. Another problem of this bath is originated from the high concentration of organic components, especially high concentration of suppressors. The inclusion of organic additives in the bath has a potential disadvantage in subsequent processing. Organic materials or their decomposition products can be incorporated into the deposit. Organic materials incorporated into the deposit can have an undesirable influence on some deposit properties in electronic applications. For instance, when solder is reflowed, incorporated organic additives may segregate to grain boundaries on the surface where they can adversely influence the mechanical properties, porosity, and/or wettability of the solder.

Accordingly, the purpose of this invention is to get the bath and process conditions for high deposition rate (4~6um/min) and smooth surface. Details are as follows.

a. Effect of bath components on deposition rate (limiting current density) through cathodic polarization : copper, sulfuric acid, chloride
b. Effect of current density on the growth shape and surface morphology
c. Effect of temperature on the growth shape and surface morphology
d. Effect of mass flow rate on the growth shape and surface morphology
e. Effect of each additive (accelerator and suppressor) on the growth shape and surface morphology
f. Effect of waveform on the growth shape and surface morphology
g. Optimization of the thickness uniformity using CFD reactor (at 4 to 6um/min)

The target deposition rate of this invention is 4~6um/min with the thickness uniformity less than 10% (3-sigma and K-value).

REDACTED

High Rate Copper for Mini-Bump Applications

[redacted] Bioh Kim

DONE

1. **Define limiting current density as a function of bath composition by cathodic polarization**
   Effect of copper, sulfuric acid, and chloride concentration
   Tested 36 kinds of baths : 4 levels of copper concentration, 3 levels of sulfuric concentration and 3 levels of chloride concentration
2. **Wafer level tests**
   Wafer level tests of bath 12 and 8 : Bath 12 showed much better results.
3. **Adjust the concentration of major components for better bath stability**
   Copper, sulfuric acid, and chloride concentration
4. **Define the relation between current density and deposition rate**
   $50\sim55 mA/cm^2 \cong 1 um/min$
   Maximum available deposition rate $\cong 5\sim6$um/min (dependent on wafer size and patterns)
5. **Surface morphology as a function of process conditions**
   Current density, flow rate, and temperature
6. **Define the effect of additives on surface morphology : components and concentration**
   Shipley B-2001 : brightener
   Shipley C-2001 : suppressor
   Shipley wetter B : wetting agent
   FC 99 : wetting agent
7. **Define the effect of waveform on the morphology**
   With additive-free bath and additive-containing bath

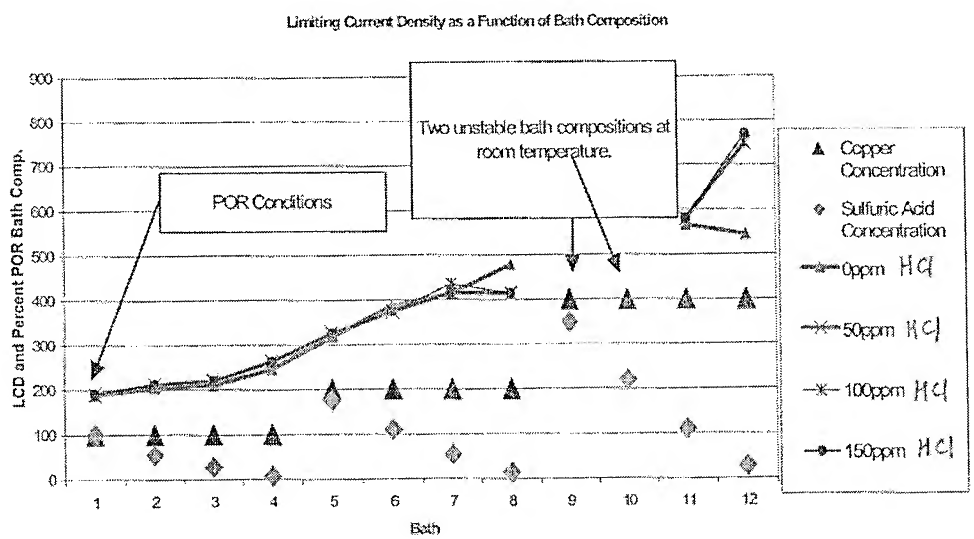
REMAINDERS

1. **Finalize bath components and composition**
   Test the effect of Enthone MD and LO on surface morphology
   (for comparing with Shipley B-2001 and C-2001)
   Test other wetting agent from Ciba (because of the discontinuation of FC series from 3M)
2. **Test effect of impinging flow at the center of wafer**
   Test new hardware to boost mass flow at the center of wafer
3. **Optimize thickness uniformity**
   With CFD reactor
4. **Setup POR : CFD reactor, deposition rate of 5~6um/min**

REDACTED

1. Effect of bath components on deposition rate (limiting current density) through cathodic polarization

To increase the operational current density of copper bump plating, the effect of process conditions on the diffusion-limited current density was investigated using copper sulfate bath. This research focused mainly on the effect of the component concentration including copper ions, sulfuric acid, and additive (chloride). In order to define the diffusion-limited current density of each system, cathodic polarization with EG&G potentiostat was utilized. The diffusion-limited current density was increased either by increasing metal concentration, by decreasing sulfuric concentration or by increasing the ratio of metal to acid.



Bath	CuSO4 g/L	Cu g/L	H2SO4 ml/L	Ratio Acid: Copper	Conductivity mS
1	62.40	15.89	82.96	7.36	416
2	62.40	15.89	52.18	5	284
3	62.40	15.89	26.09	3	160
4	62.40	15.89	6.52	1.5	54
5	124.80	31.77	165.92	7.36	559
6	124.80	31.77	104.35	5	456
7	124.80	31.77	52.18	3	272
8	124.80	31.77	13.04	1.5	86
9	249.60	63.55	331.84	7.36	557
10	249.60	63.55	208.71	5	637
11	249.60	63.55	104.35	3	416
12	249.60	63.55	26.09	1.5	151

Define limiting current density by plating

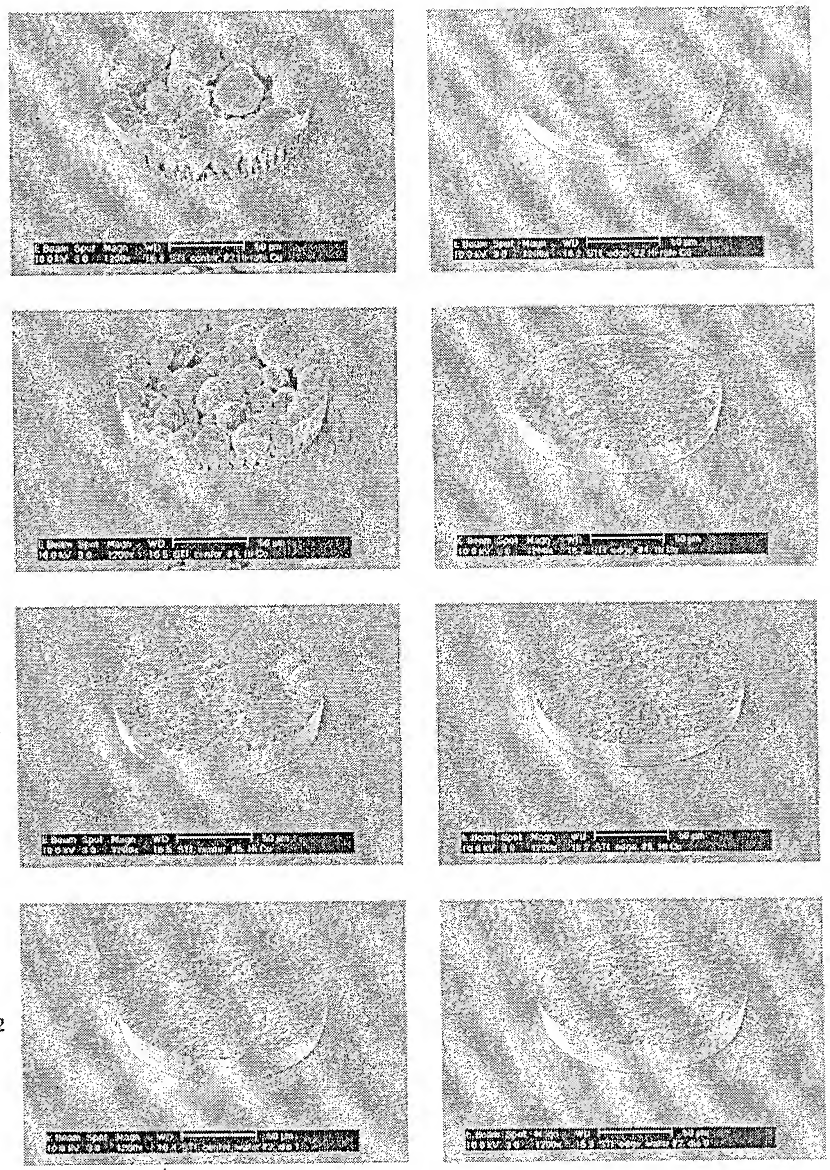
Bath 12 (with 50ppm HCl), BDTV1 wafers, 5.5GPM, 60RPM, 25°C, No oscillation

430mA/cm^2

370mA/cm^2

335mA/cm^2

225mA/cm^2



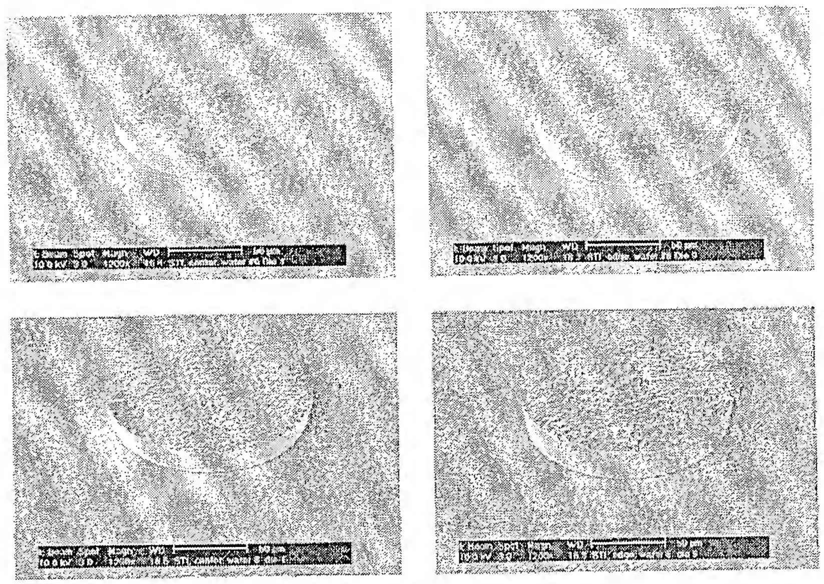
Center Edge

In this condition, the limiting current density was found above 335mA/cm^2. As the center of the wafer has low mass transport rate, this area reached the limiting current density earlier than other areas.

Bath 8 (with 50ppm HCl), BDTV1 wafers, 5.5GPM, 60RPM, 25°C, No oscillation

225mA/cm^2

168mA/cm^2



Center Edge

In this condition, the limiting current density was found above 225mA/cm^2.

2. Effect of current density on the growth shape and surface morphology
   (with conventional reactor and modified bath 12)

   With increasing the current density,

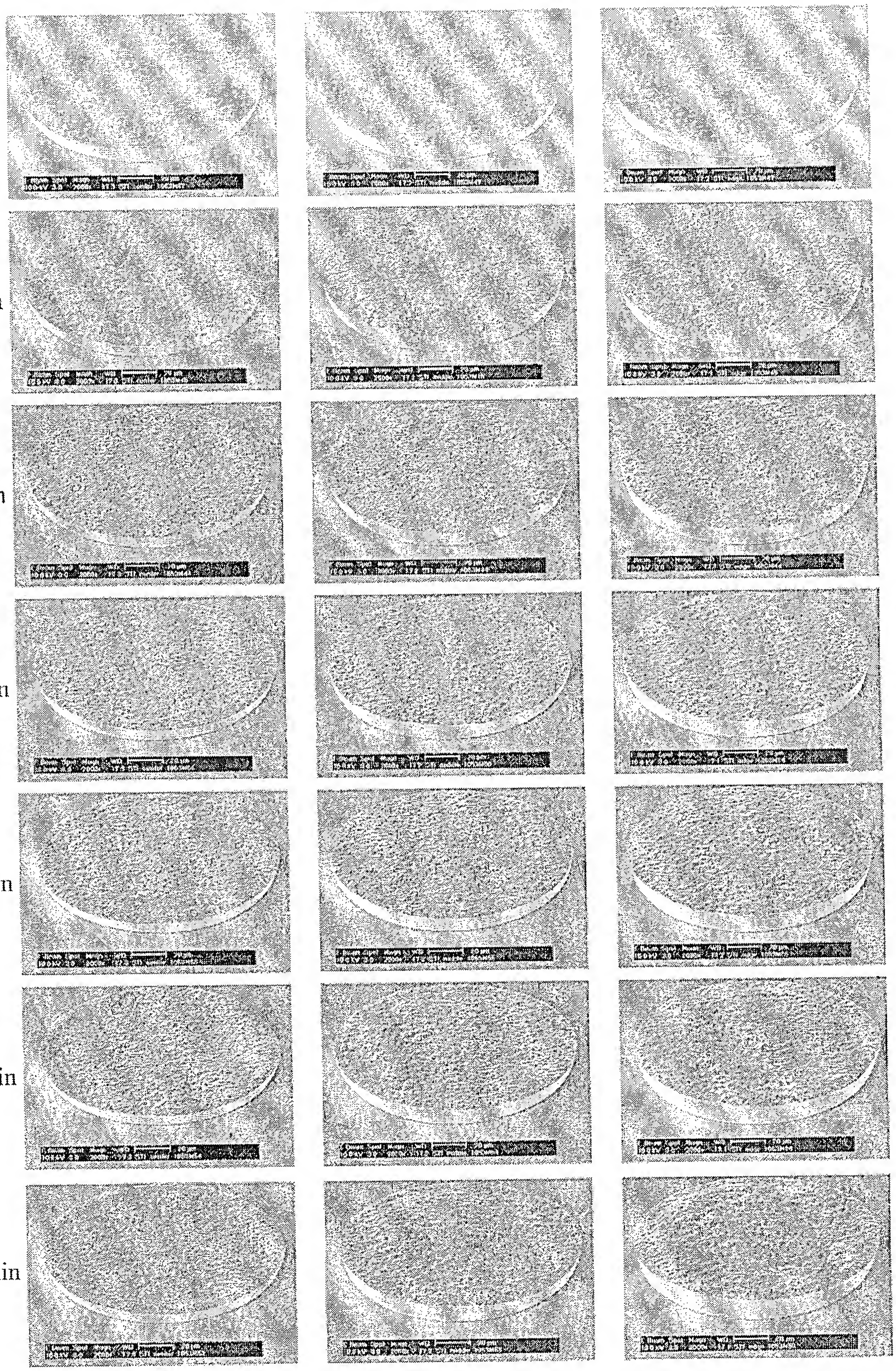
   a. The growth mechanism was more affected by mass transport
      ; waviness of surface and increased thickness deviation between center and edge
   b. The surface became smoother.

   Bath

   a. Copper sulfate : 250g/L
   b. Sulfuric acid : 65g/L
   c. HCl : 50ppm

   Process Conditions

   a. 5.5 GPM
   b. 60 RPM
   c. 25 °C
   d. No oscillation (in order to see the effect of mass flow direction)
   e. POR diffuser
   f. BDTV2 wafers



1um/min
2um/min
3um/min
4um/min
5um/min
6um/min
7um/min

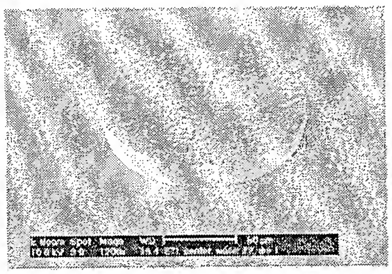
Center | Middle | Edge

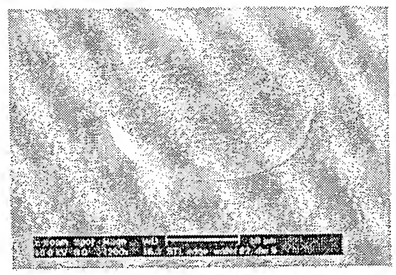
3. Effect of temperature on the growth shape and surface morphology (with conventional reactor)

Process Conditions : 5.5 GPM, 60 RPM, No oscillation, POR diffuser, BDTV1 wafers

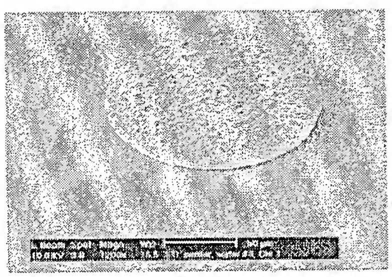
Bath 12, >4um/min

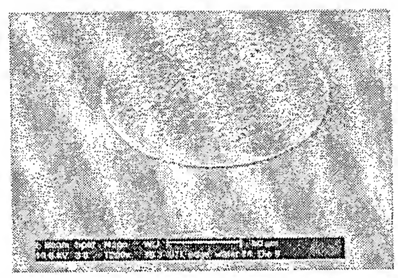
25°C





50°C

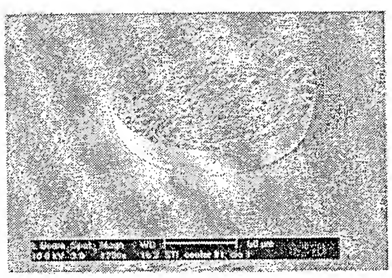


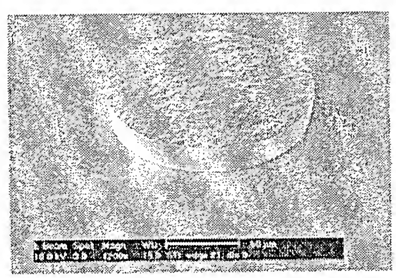


Center | Edge

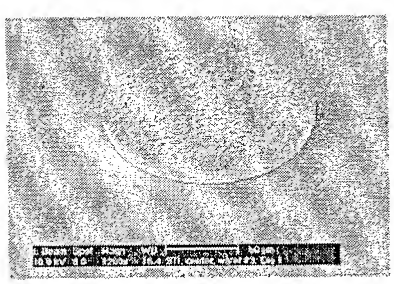
Bath 12, >6um/min

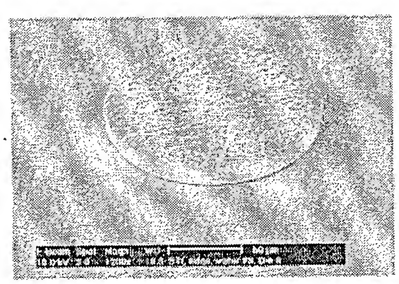
25°C





50°C



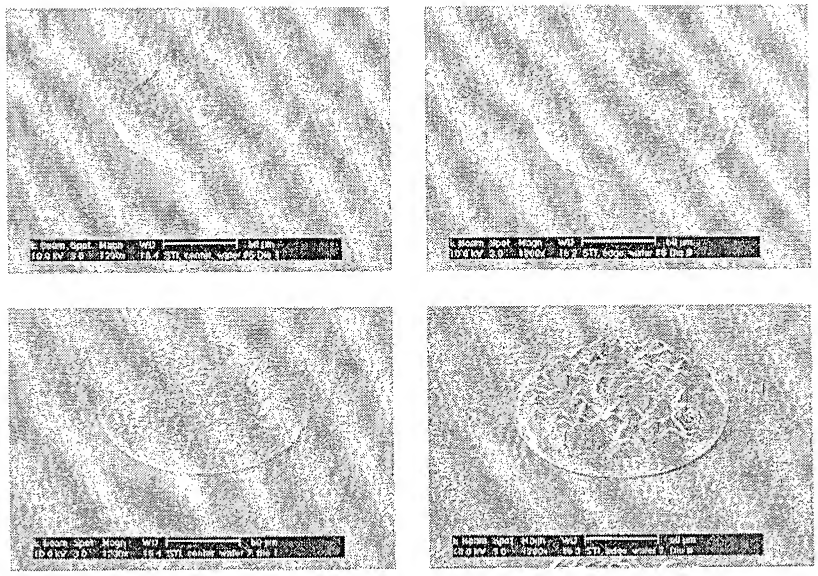


Center | Edge

Bath 8, >4um/min

25°C

50°C

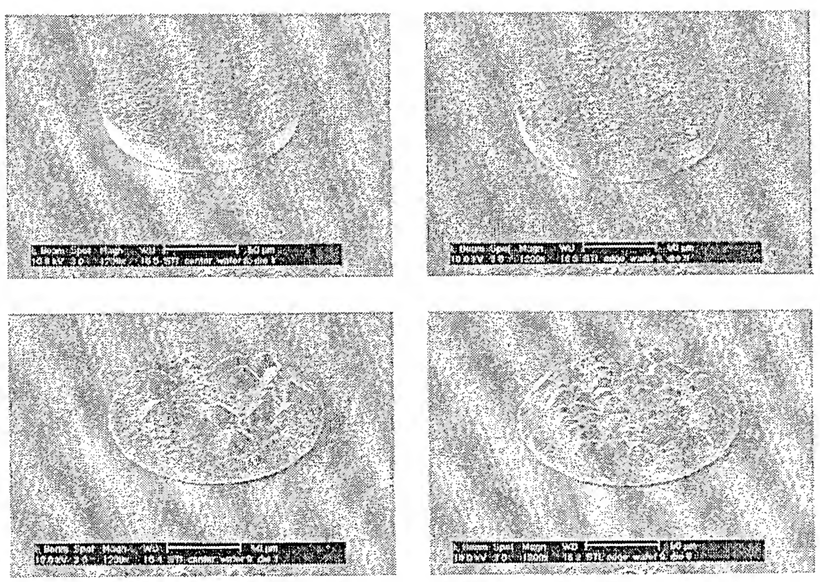


Center Edge

Bath 8, >3um/min

25°C

50°C

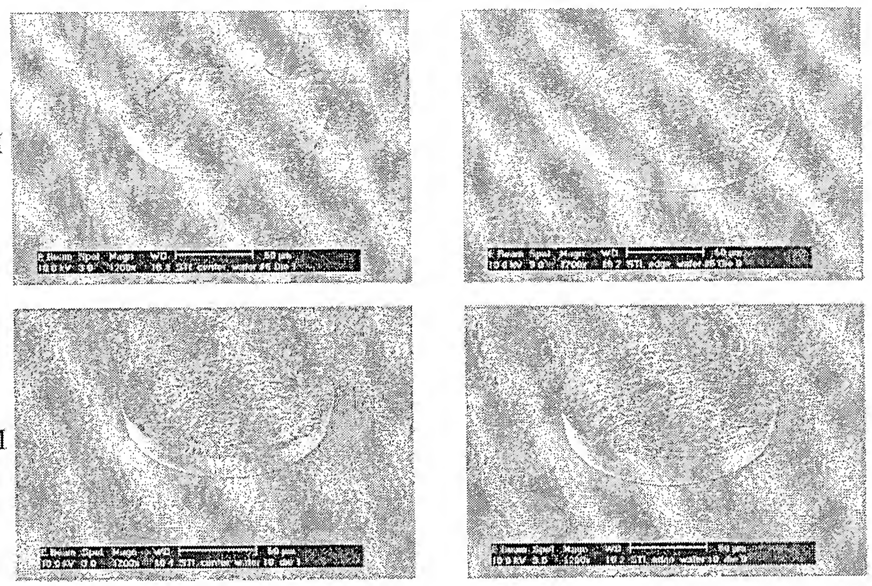


Center Edge

As can be seen from the above figures, the difference between center and edge was reduced, but the rougher surface was obtained at high temperature.

4. Effect of mass flow rate on the growth shape and surface morphology (with conventional reactor)

Process Conditions : 60 RPM, 25 °C, No oscillation, POR diffuser, BDTV1 wafers, Bath 8



5.5 GPM

8.0 GPM

Center | Edge

As can be seen from the above figures, there was no significant effect of mass flow rate on the morphology, because 5.5 gpm is already high enough.

5. Effect of additives on the growth shape and surface morphology
   (with conventional reactor)

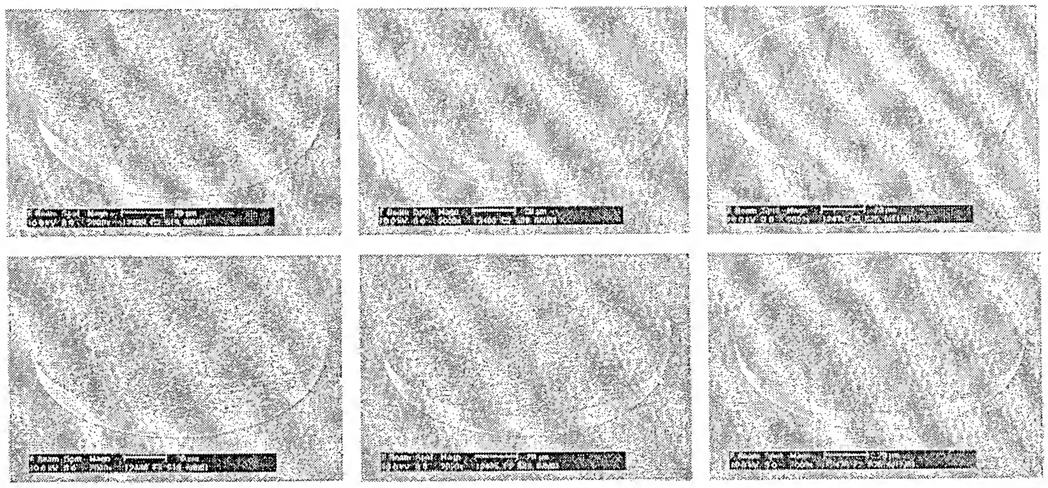
   Process Conditions : 6GPM, 60RPM, 30°C, 20 second oscillation, modified diffuser, BDTV1 wafers, modified bath 12

   Bath
   a. Copper sulfate : 250g/L
   b. Sulfuric acid : 65g/L
   c. HCl : 50ppm
   d. FC99 : 2ml/L

   As can be seen from the figures,
   a. Additive free bath : rough surface
   b. Bath containing accelerator : smoother but not regular
   c. Bath containing accelerator and suppressor : much smoother but crater formation, resist changed hydrophobic after plating, resulting in the difficulty of consecutive plating

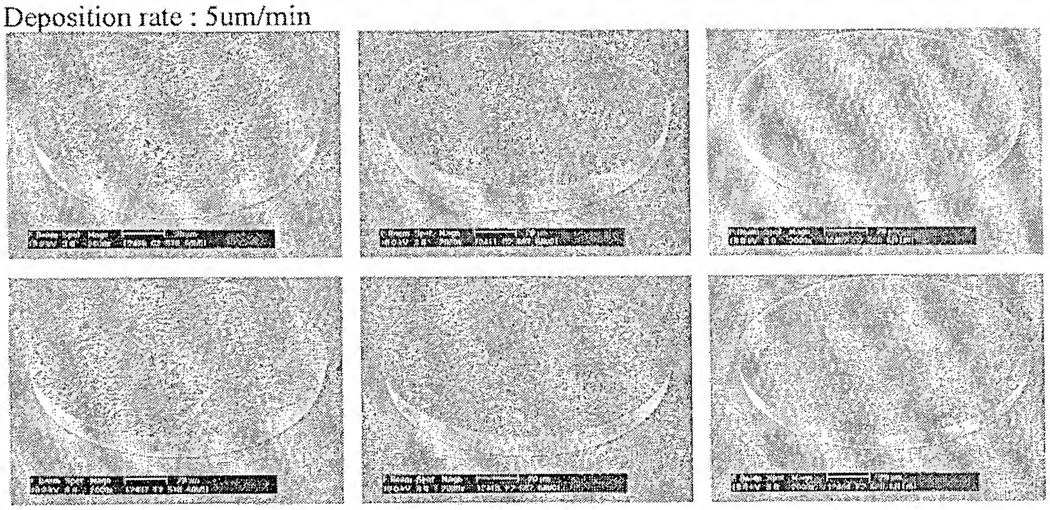
Deposition rate : 4um/min

Center
Edge



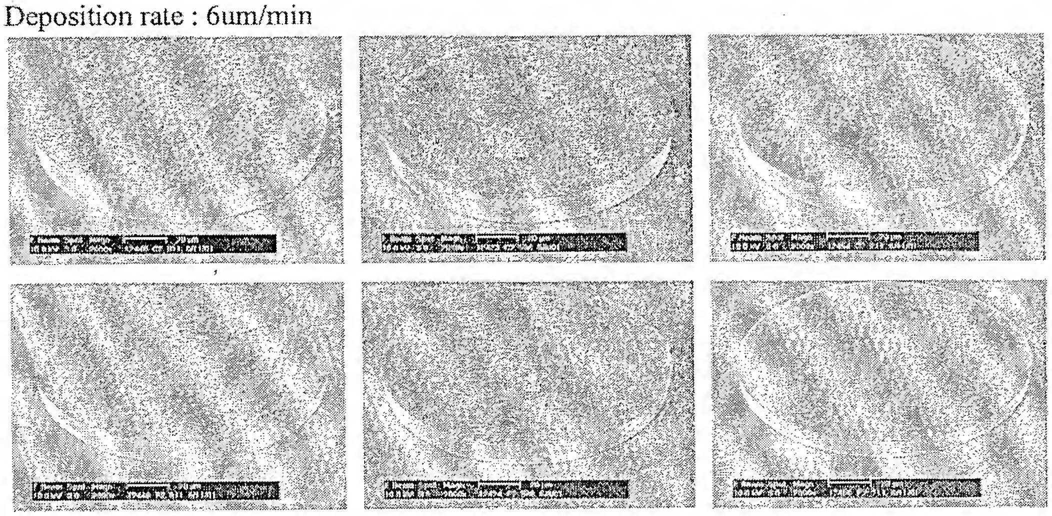
Deposition rate : 5um/min

Center
Edge



Deposition rate : 6um/min

Center
Edge



No Additives | With accelerator (Shipley B2001 3ml/L) | With accelerator and suppressor (Shipley B2001 3ml/L+ Shipley C2001 22m/L)

Effect of the concentration of accelerator on surface morphology

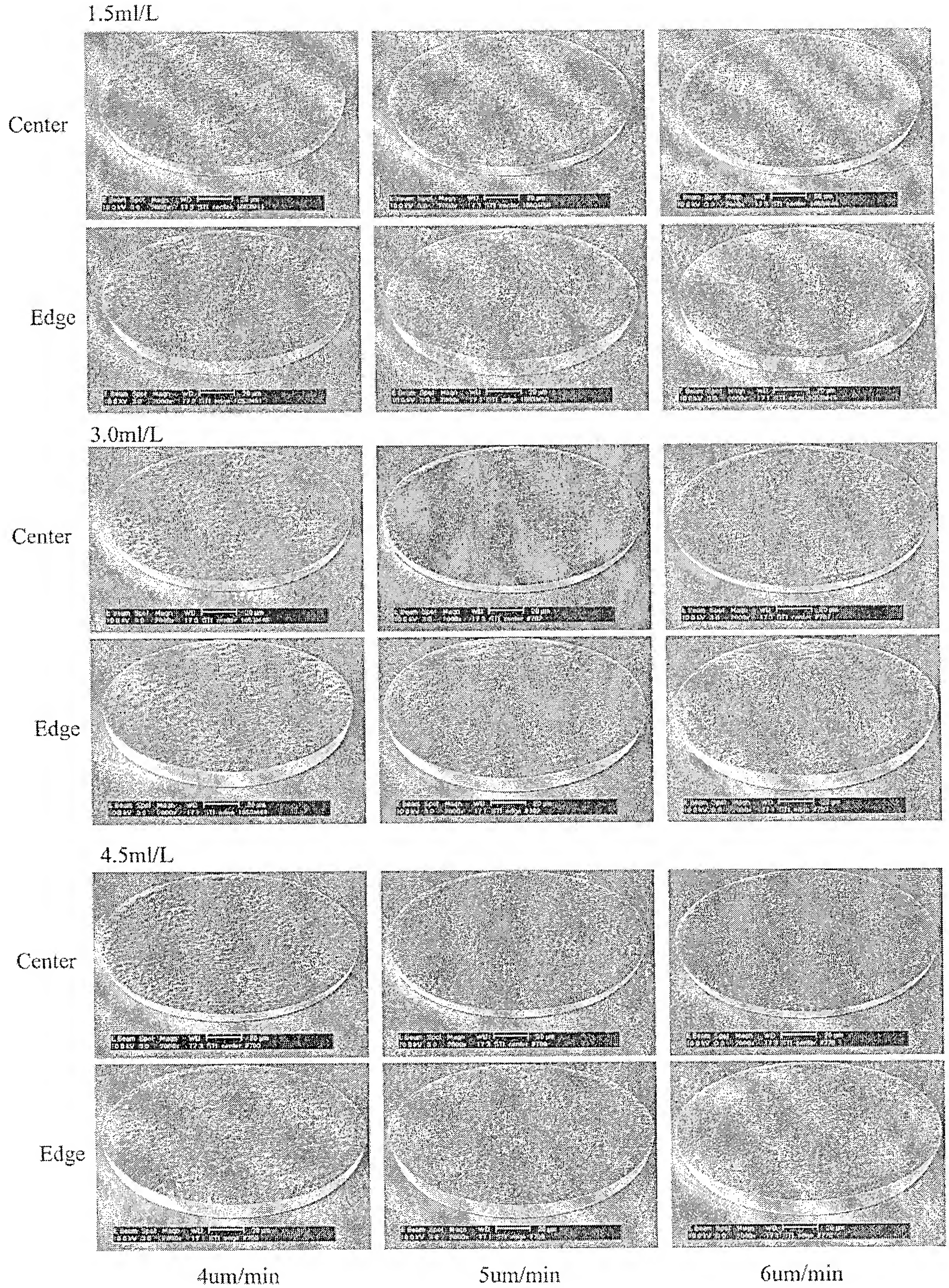
Process Conditions : 5.5GPM, 60RPM, 25°C, No oscillation, standard diffuser, BDTV2 wafers, modified bath 12

Bath

a. Copper sulfate : 250g/L
b. Sulfuric acid : 65g/L
c. HCl : 50ppm
d. B2001 : 1.5, 3.0 and 4.5ml/L

As the bath that contains accelerator looks promising, the effect of accelerator concentration was tested with another type of wafers. The results said the effect of concentration is negligible.

As can be seen, the surface is quite smooth, but still has macroscopic roughness on the surface.


1.5ml/L
Center
Edge
3.0ml/L
Center
Edge
4.5ml/L
Center
Edge
4um/min
5um/min
6um/min

6. Effect of waveform on the growth shape and surface morphology (with conventional reactor)

Process Conditions : 6GPM, 60RPM, 30°C, 20 second oscillation, modified diffuser, BDTV1 wafers, modified bath 12

Bath

a. Copper sulfate : 250g/L
b. Sulfuric acid : 65g/L
c. HCl : 50ppm
d. FC99 : 2ml/L

Effect of pulse condition can be summarized as follows.

a. In case of additive-free bath, the surface became more faceted and rougher by using pulse plating.
b. In case of accelerator-containing bath, the surface became smoother by using proper pulse conditions.
c. In case of suppressor-containing bath, the surface morphology looks better by pulse plating. The surface irregularity (waviness, crater) was not significantly improved by changing waveform.

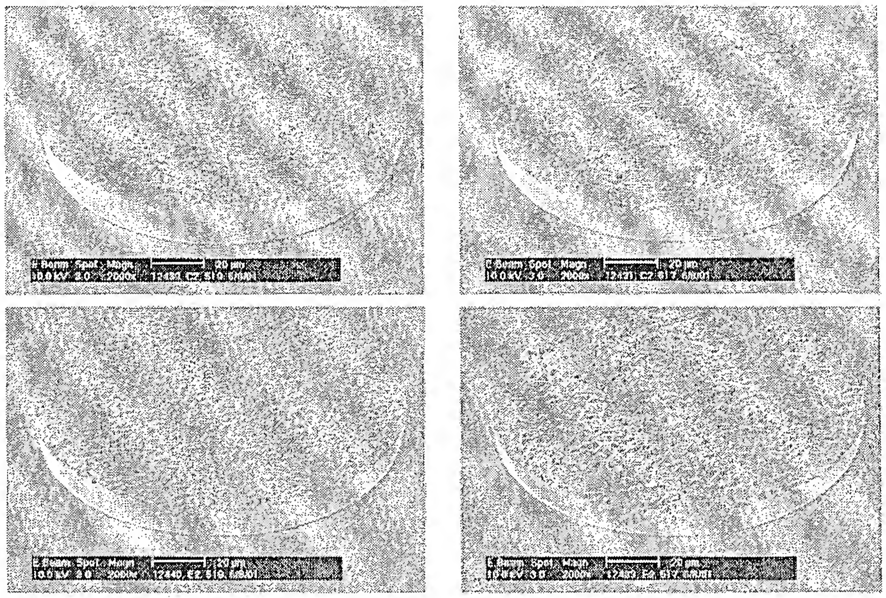
From the results so far, the best morphology can be obtained by pulse plating with accelerator-containing bath. In case of suppressor containing bath, the resulting high concentration of impurity in the film can adversely influence the mechanical properties, porosity, and/or wetability of the solder. The change of resist surface (hydrophilic to hydrophobic) can make another dewetting problem in case of consecutive plating. (for example, cu/solder)

Additive-free bath

4um/min

Center

Edge

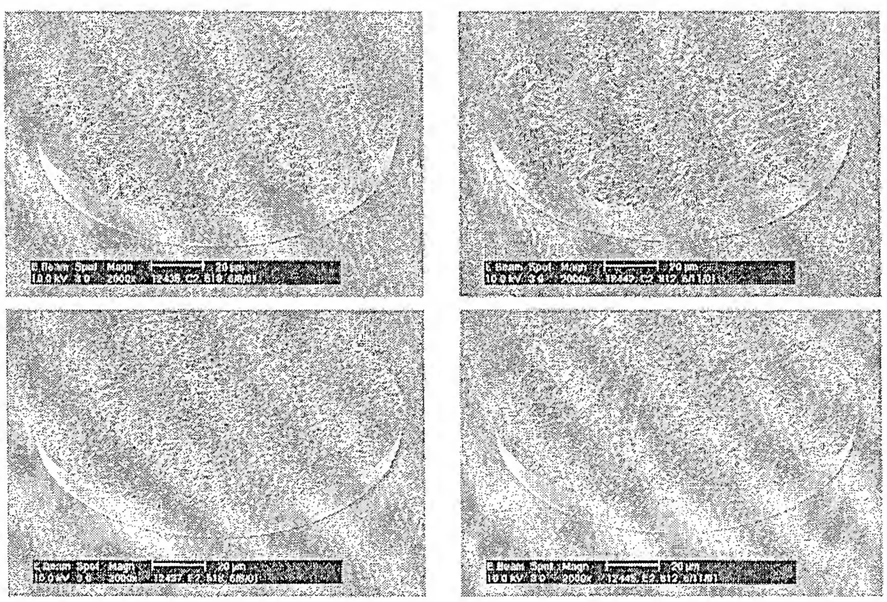


DC | 20%, 100Hz

5um/min

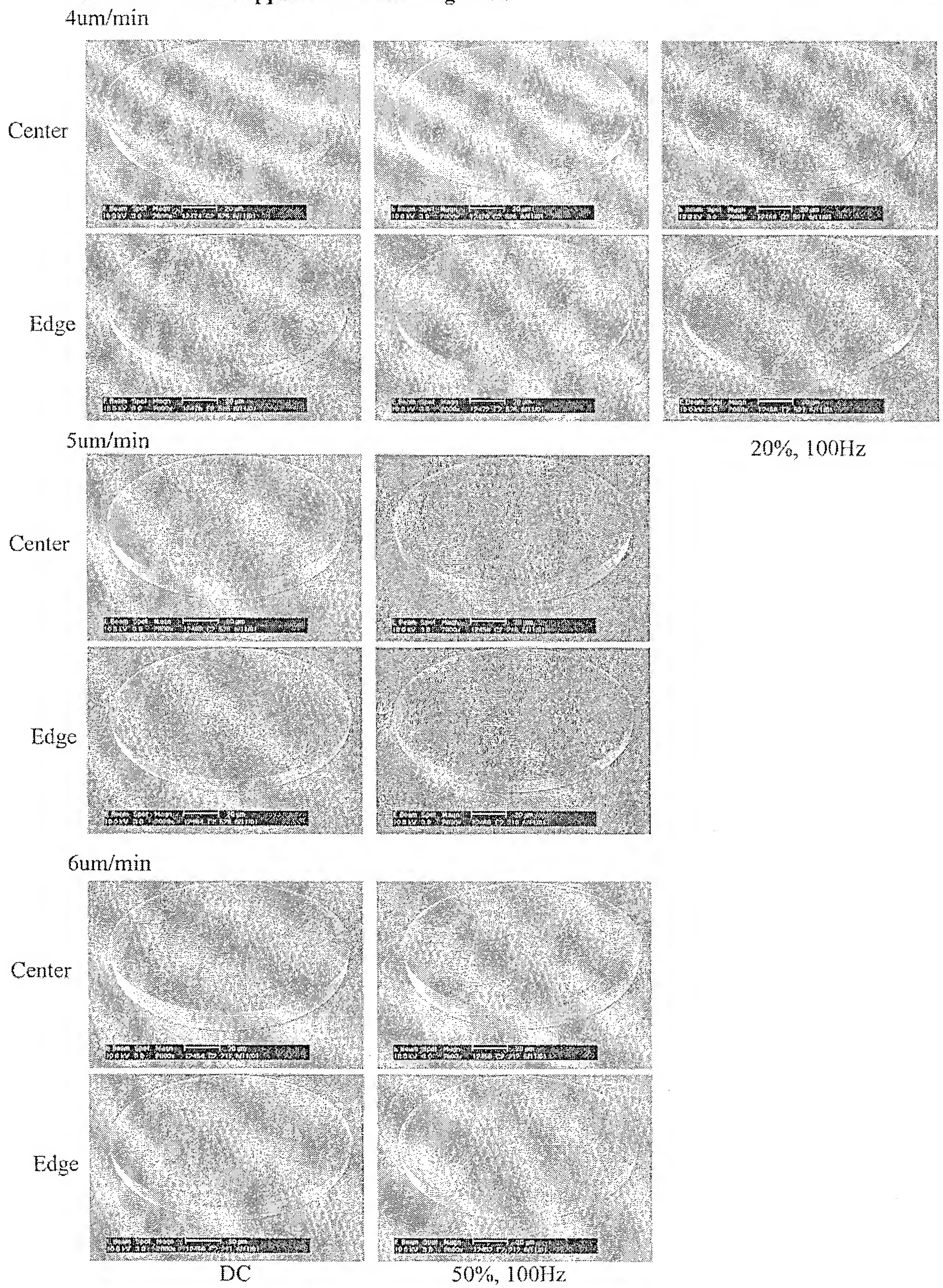
Center

Edge



DC | 50%, 100Hz

Accelerator and Suppressor-Containing Bath

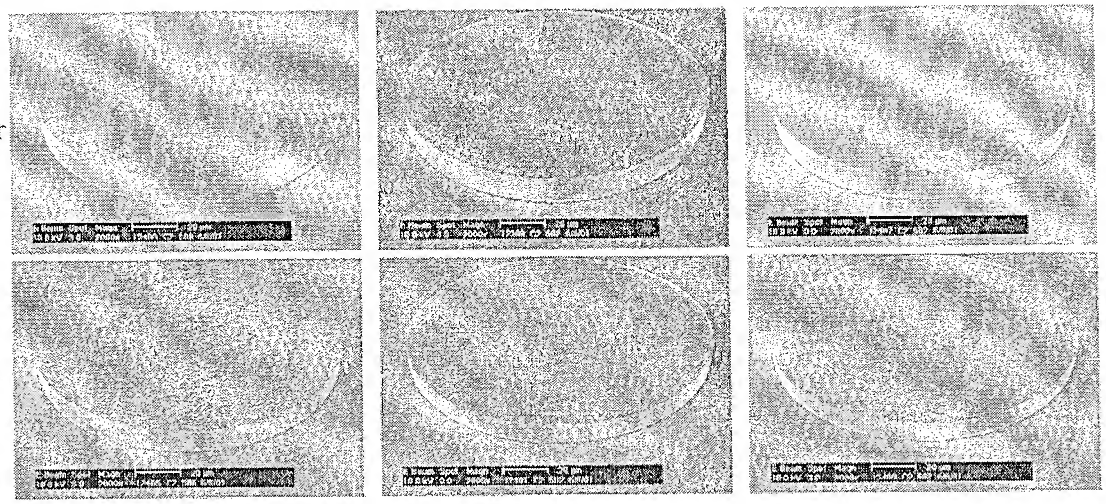


Accelerator-containing bath

4um/min

Center

Edge

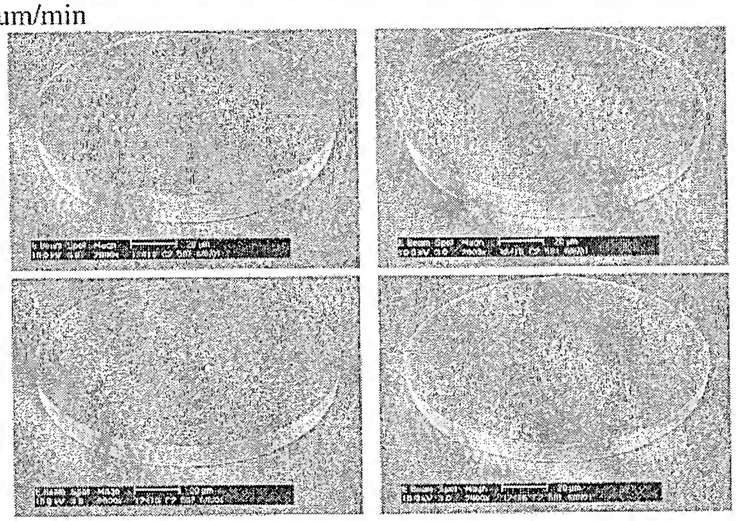


20%, 100Hz

5um/min

Center

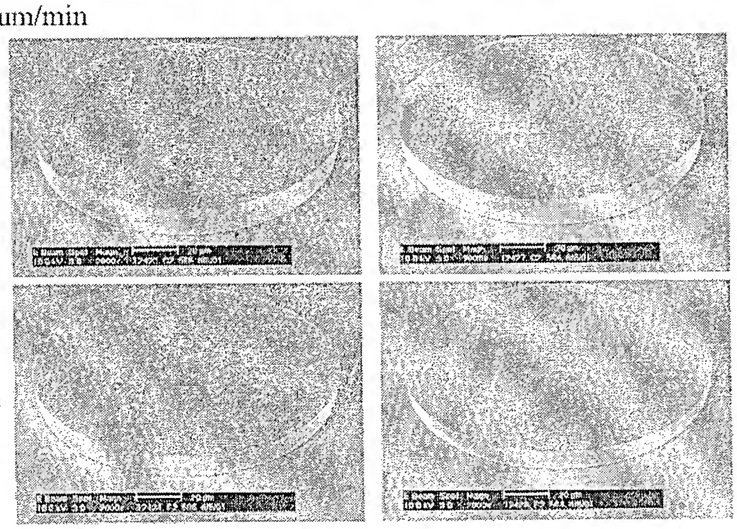
Edge



6um/min

Center

Edge



DC

50%, 100Hz